



# Deposition and dielectric characterization of strontium and tantalum-based oxide and oxynitride perovskite thin films



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## ABSTRACT

We have synthesized the composition  $x = 0.01$  of the  $(\text{Sr}_{1-x}\text{La}_x)_2(\text{Ta}_{1-x}\text{Ti}_x)_2\text{O}_7$  solid solution, mixing the ferroelectric perovskite phases  $\text{Sr}_2\text{Ta}_2\text{O}_7$  and  $\text{La}_2\text{Ti}_2\text{O}_7$ . Related oxide and oxynitride materials have been produced as thin films by magnetron radio frequency sputtering. Reactive sputter deposition was conducted at  $750^\circ\text{C}$  under a 75 vol.% (Ar) + 25 vol.% ( $\text{N}_2, \text{O}_2$ ) mixture. An oxygen-free plasma leads to the deposition of an oxynitride film  $(\text{Sr}_{0.99}\text{La}_{0.01})(\text{Ta}_{0.99}\text{Ti}_{0.01})\text{O}_2\text{N}$ , characterized by a band gap  $E_g = 2.30$  eV and a preferential (001) epitaxial growth on (001)  $\text{SrTiO}_3$  substrate. Its dielectric constant and loss tangent are respectively  $\text{Epsilon}' = 60$  (at 1 kHz) and  $\text{tanDelta} = 62.5 \times 10^{-3}$ . In oxygen-rich conditions (vol.%  $\text{N}_2 \leq 15\%$ ), (110) epitaxial  $(\text{Sr}_{0.99}\text{La}_{0.01})_2(\text{Ta}_{0.99}\text{Ti}_{0.01})_2\text{O}_7$  oxides films are deposited, associated to a larger band gap value ( $E_g = 4.55$  eV). The oxide films permittivity varies from 45 to 25 (at 1 kHz) in correlation with the decrease in crystalline orientation; measured losses are lower than  $5.10^{-3}$ . For  $20 \leq \text{vol.}\% \text{N}_2 \leq 24.55$ , the films are poorly crystallized, leading to very low permittivities (minimum  $\text{Epsilon}' = 3$ ). A correlation between the dielectric losses and the presence of an oxynitride phase in the samples is highlighted.

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## 1. Introduction

Among perovskite materials, many original compounds are synthesized from two parent phases, in the form of solid solutions in which the perovskite structure is maintained through cationic substitutions. The aim is to control one or more properties of the material by varying its chemical composition. Ferroelectric perovskite compounds, such as  $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$  (PZT) [1],  $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$  (BST) [2] or  $\text{KTa}_x\text{Nb}_{1-x}\text{O}_3$  (KTN) [3], were thus developed with the objective of bringing their Curie temperature ( $T_C$ ) near room temperature, and therefore, benefit from high values of permittivity, adjustable via an external DC electrical field. The latter property can be used to make frequency agile antennas, i.e. antennas whose resonance frequency can be varied and consequently be used in different standards [4,5]. In miniature antennas, high permittivity perovskite thin films are positioned as the substrate of planar metallic antennas or are integrated in localized components such as capacitances [6]. Agility and miniaturization are two applications

targeted for the materials presented in this paper.

$\text{Sr}_2\text{Ta}_2\text{O}_7$  and  $\text{La}_2\text{Ti}_2\text{O}_7$ , which crystallize in non-centrosymmetric space groups  $\text{Cmc}2_1$  and  $\text{P}2_1$  respectively, are perovskite ferroelectric compounds:  $\text{Sr}_2\text{Ta}_2\text{O}_7$  with  $T_C = -107^\circ\text{C}$  [7] and  $\text{La}_2\text{Ti}_2\text{O}_7$  with  $T_C = 1466^\circ\text{C}$  [8]. Cross-substitution on the A and B sites of the prototype layered perovskite structure (PLS)  $\text{A}_2\text{B}_2\text{O}_7$  would result in the solid solution  $(\text{Sr}_{1-x}\text{La}_x)_2(\text{Ta}_{1-x}\text{Ti}_x)_2\text{O}_7$ . Here, we have interpolated the results of Nanamatsu et al. on single crystals and ceramics [7] and determined the stoichiometry  $x \sim 0.01$  giving a value of  $T_C$  close to room temperature. The present paper deals with the synthesis of the  $(\text{Sr}_{0.99}\text{La}_{0.01})_2(\text{Ta}_{0.99}\text{Ti}_{0.01})_2\text{O}_7$  (SLTTO) compound as thin films deposited by radio-frequency (rf) reactive magnetron sputtering. Moreover, we were interested in the deposition of the oxynitride  $(\text{Sr}_{0.99}\text{La}_{0.01})(\text{Ta}_{0.99}\text{Ti}_{0.01})\text{O}_2\text{N}$  (SLTTON) compound, where substitution occurs on the anionic sublattice because of similar values of ionic radii and electronegativity for oxygen and nitrogen ( $r_{\text{O}^{2-}} = 1.40 \text{ \AA}$ ;  $r_{\text{N}^{3-}} = 1.50 \text{ \AA}$ ;  $\chi_{\text{O}} = 3.44$ ;  $\chi_{\text{N}} = 3.04$ ). Oxynitride perovskites are currently studied because of their original properties compared to their oxide parents, in particular an absorption in the visible domain leading to their use as photocatalyst in the water-splitting reactions [9,10], and very high permittivities

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[11–14], with a potential use in agile and/or miniaturized antennas. Some reports concern these oxynitride compounds in the form of thin films [15–17].

In recent years, our research has been concerned with the deposition of oxide and oxynitride perovskite films for a use in electronic and telecommunication devices such as antennas. We have recently reported on SLTTO and SLTTON films deposited by reactive rf magnetron sputtering using Ar + O<sub>2</sub> or Ar + N<sub>2</sub> plasma, respectively [18]; the resulting films were epitaxially grown on (001) MgO substrates. The objective of the present study is to determine whether a mixture of the SLTTO and SLTTON compounds could be obtained using an original reactive plasma, containing Ar and both O<sub>2</sub> and N<sub>2</sub>. Considering that free energies of formation of oxide compounds are lower than those of oxynitrides [19], this sort of dual-reactive medium has rarely been used up to now for the deposition of films using an oxide precursor [20]. Usually, on powders, an oxide precursor exposed to an oxidizing and nitriding atmosphere leads to a stable oxide, whereas an (oxy)-nitride or metallic precursor under an oxidizing and nitriding atmosphere (O<sub>2</sub>/N<sub>2</sub>, for example [21]) can lead to an original oxynitride material. Here, the synthesis of the compounds as thin films, using an energetic deposition process such as sputtering deposition under dual-reactive plasma, allows us to consider that this (oxy)nitride synthesis route could be tested. Furthermore, as detailed hereafter, the mixing of SLTTO and SLTTON materials was intended in order to reduce the dielectric loss of films.

Given the very small amount (1%) of the La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> material in the synthesized compounds, we will discuss our results in reference to closest compounds, Sr<sub>2</sub>Ta<sub>2</sub>O<sub>7</sub> and SrTaO<sub>2</sub>N. For Sr<sub>2</sub>Ta<sub>2</sub>O<sub>7</sub>, permittivities from 20 to 95 have been measured on thin films [22–24]; the dispersion of values can be explained by the different methods of film deposition (atomic vapor deposition, sol–gel), crystallization (amorphous, polycrystalline) and thickness of films (from 15 to 250 nm). The available data on SrTaO<sub>2</sub>N dielectric performance are scarce; on bulk samples, permittivities close to 3000 have been published by Kim et al. [11] and Hinuma et al. [12], while Masubuchi et al. reported very recently on permittivities in the range 60–200 for ceramics obtained by high pressure densification [13]. On thin films, Oka et al. reported on SrTaO<sub>2</sub>N films deposited by nitrogen plasma enhanced-laser ablation [25]. These films were epitaxially grown on conducting niobium-doped (001) SrTiO<sub>3</sub> substrates and reveal permittivity around 2000 at 1 kHz at room temperature, with dielectric losses tanδ close to 35 × 10<sup>−3</sup>. PFM measurements also pointed out the piezoelectric and ferroelectric behavior of films; Oka et al. proposed the material to be constituted of a relaxor ferroelectric-type matrix surrounding classical ferroelectric-type nano-domains. Besides these studies, we have also published on oxynitride LaTiO<sub>2</sub>N (LTON) films; their permittivities are dependent on their structure and microstructure (κ<sub>LTON</sub> ~ 375–1220 [26,27]), but are always higher than the La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> (LTO) oxide (κ<sub>LTO</sub> ~ 60 [28,29]). The drawback lies in higher losses, with tanδ from 0.06 to 1 for LTON thin films. For this reason, the present study does not only concern the synthesis of SLTTO oxide and SLTTON oxynitride, but the possibility of producing mixtures of phases, or even forming a (Sr<sub>0.99</sub>La<sub>0.01</sub>)<sub>2</sub>(Ta<sub>0.99</sub>Ti<sub>0.01</sub>)<sub>2</sub>(O,N)<sub>7</sub> (SLTT) solid solution and thereby modulate the nitrogen content in films and so, reduce the dielectric losses. For that purpose, we conducted a series of deposits using an original reactive sputtering gas composed of 75 vol.% of argon and 25 vol.% of dioxygen and dinitrogen. This paper deals with the deposition of such samples; it presents the structural and microstructural characterization of the oxide and oxynitride deposited films and gives the first results of their dielectric characterization at room temperature in the low frequency range. The study concerning the ferroelectric properties, in particular their temperature dependence, will concern other

samples and will be presented in a separate paper.

## 2. Materials and methods

Film deposition is carried out using rf reactive magnetron sputtering in a Plassys MP450S reactor using a homemade (Sr<sub>0.99</sub>La<sub>0.01</sub>)<sub>2</sub>(Ta<sub>0.99</sub>Ti<sub>0.01</sub>)<sub>2</sub>O<sub>7</sub> target. This is obtained by uniaxial compaction of SLTTO powder synthesized by solid state chemical route from stoichiometric amounts of SrCO<sub>3</sub>, Ta<sub>2</sub>O<sub>5</sub>, La<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> heated under air at 1400 °C during 30 h. X-ray diffraction (XRD) analysis confirms the crystallization of the powder according to a Sr<sub>2</sub>Ta<sub>2</sub>O<sub>7</sub> analog (see [Supplementary Data 1](#)).

A series of films is deposited using the same sputtering conditions, except the gas mixture. The plasma mixture always contains 75vol.% of argon plus 25vol.% dedicated to the reactive part, i.e. x vol.%N<sub>2</sub> + y vol.%O<sub>2</sub>, with x + y = 25; deposited films will be labeled as SLTT-xN<sub>2</sub>-yO<sub>2</sub> (for example, SLTT-2.5N<sub>2</sub>-22.5O<sub>2</sub> has been deposited under a mixture of vol.%N<sub>2</sub> = 2.5 and vol.%O<sub>2</sub> = 22.5). The other deposition parameters are the following: total pressure p<sub>T</sub> = 40 mTorr; rf power P<sub>rf</sub> = 90 W (2.04 W/cm<sup>2</sup>); substrate temperature T<sub>S</sub> = 750 °C and target–substrate distance d = 5 cm. Before deposition, a pre-sputtering of the target is performed during 100 min under the same gas mixture than deposition. The films are cooled under the same gas mixture than deposition; no post-annealing is performed.

Two kinds of single-crystalline substrates are used: (001) MgO and (001) Nb:SrTiO<sub>3</sub>. The MgO substrate is used to determine the band-gap of the film from UV–visible spectra, while conducting Nb(1.4%):SrTiO<sub>3</sub> is preferred to make Metal - Insulating - Metal (MIM) structures for the dielectric measurements.

During deposition, the plasma is monitored by Optical Emission Spectroscopy (OES) using an Ocean Optics HR4000 monochromator, with the position of the optical fiber kept constant from one experiment to another. The emissions of Ar and N<sub>2</sub> are followed at 750.4 nm (2p<sub>1</sub> → 1s<sub>2</sub>) [30] and 357.0 nm (C<sup>3</sup>Π<sub>u</sub> → B<sup>3</sup>Π<sub>g</sub>) [31] respectively. In order to decrease the effect of the variation of the electron temperature, the N<sub>2</sub> band intensity is divided by the one of the Ar line.

Thickness of layers is measured by Scanning Electron Microscope (SEM) cross-sectional view, using a JEOL 5440 SEM; error on thickness value is estimated as being lower than 20 nm. The chemical composition of samples is determined by semi-quantitative Energy Dispersive Spectrometry (EDS) in the JEOL 5440 SEM operating at 20 kV; lower limit of detection is around 2 at.%. UV–Visible transmittance spectra are collected by a Perkin–Elmer Lambda 20 spectrometer operating in the range [200–1100] nm. Assuming direct transitions, band-gap values are obtained using the relation:

$$(\alpha h\nu)^2 = (h\nu - E_g)2$$

where  $h\nu$  is the photon energy. Hence plotting  $(\alpha h\nu)^2$  as a function of  $h\nu$ , the extrapolation of the linear region at zero gives the value of  $E_g$ . The error is estimated as 0.05 eV.

X ray diffractograms are collected using a Seifert XRD 3003 diffractometer with a copper anode. Conventional  $\theta - 2\theta$  and  $\phi$  scans are recorded. In order to quantify the thin film orientation, the Lotgering factor is used. This factor compares the orientation of a thin film versus randomly oriented material (i.e. powder) and is able to vary from 0 for a non-oriented layer to 1 for a total oriented layer. The Lotgering factor is calculated using the relations [32]:

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